A rising mismatch between system complexity, characterization, and theory in electrocatalysis: challenges and solutions

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ABSTRACT

Electrocatalytic systems are enormously challenging to understand. Nevertheless, the complexity of systems reported in the literature constantly increases, with frequent reports on heterostructured electrodes containing multiple interfaces. As current electrochemical and analytical methods can hardly meet this complexity, fundamental catalytic aspects often remain elusive, e.g., intrinsic activity, number of active sites, surface area, in-situ structure, etc. Nonetheless, complex interface-related hypotheses are postulated. Herein, we describe a pathway with essential electrocatalytic and analytical points that must be addressed before meaningful ab initio (mainly density functional theory, DFT) models and new hypotheses are raised. It comprises three parts: (i) determining if the activity changed intrinsically, (ii) revealing the in-situ composition, and (iii) identifying the active sites and the reaction mechanism. We anticipate that this perspective helps authors and reviewers acknowledge electrocatalysis' tremendous complexity and provides a systematic pathway to check if fundamental aspects are covered before complex, potentially misleading hypotheses are raised.

1. Introduction

Electrocatalysis is critical to decarbonizing society. [1] Thus, in the last decade, every year, thousands of reports have been published on topics like water splitting, the hydrogen and oxygen evolution reaction (HER and OER), the oxygen reduction and hydrogen oxidation reaction (ORR and HOR), and the electrocatalytic conversion of biomass, e.g., the oxidation of 5-(hydroxymethyl)furfural or glycol. [1–3] In order to find novel and better-performing catalysts for these highly desired reactions, the complexity of the reported system is continuously increasing, e.g., by combining multiple phases and interfaces. In this regard, even a powder catalyst loaded on a non-innocent nickel foam substrate is a complex interface containing electrode. Such systems frequently show remarkable electrocatalytic activities. [4] To understand the cause of the electrocatalytic performance, density functional theory (DFT) calculations are commonly performed on small model systems, e.g., an interface assumed to be responsible for catalysis. In the end, one to three parameters apparently explaining the observed activity differences are identified, such as interfacial electron redistribution, [5] a Mott-Schottky junction with local charge polarization, [6] shape-enhanced electric fields, [7] hydrophilicity, [4] free electrons at

the heterointerface, [8] and many others complex hypotheses. Thus, with the current literature, for every possible result, a wide range of reported, partly contradicting explanations can be found. While this practice suggests that even complex systems can be easily understood with basic characterizations and a DFT calculation, the scientific community cannot even unambiguously resolve the mechanism and active sites of, e.g., the OER on bimetallic nickel-iron-based or even monometallic cobalt-based catalysts. [9–12] We found that explaining the activity difference between simple cobalt oxides requires many parameters. [13] Furthermore, with the current surface area and the number of active site determination methods, it is exceptionally challenging to determine the intrinsic activity of simple systems. [14,15] These challenges often create a mismatch between system complexity, characterizations, and theory, slowing down the progress of the field, creating confusion, especially among students, and resulting in a proliferation of misleading, meaningless, and oversimplified conclusions. [2].

Another challenge of electrocatalysis is that the initially designed materials (precatalysts/precursors) reconstruct into other phases, especially at the surface where the catalysis mostly occurs. [16–19] The reconstructed phase can be a minute part of the sample but still responsible for the catalytic activity. An example of extensive

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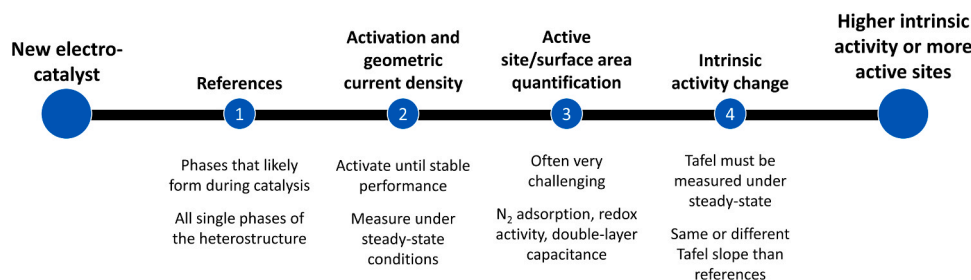*E-mail addresses:* prashanth.menezes@helmholtz-berlin.de, prashanth.menezes@mailbox.tu-berlin.de (P.W. Menezes).

Fig. 1. Intrinsic activity versus number active sites. Four points to determine if the intrinsic activity or the number of active sites causes an increased electrocatalytic performance of the investigated new electrocatalyst compared to reference samples. From our point of view, most newly reported systems achieve activity enhancements by exposing more active sites of a known catalyst, e.g., CoS nanoparticles on carbon nanotubes reconstruct during the OER into CoOOH with more available active sites than a less complex reference CoOOH. In such cases, DFT adsorption energy calculations are not required to understand the activity enhancement.

precatalyst reconstruction is the OER, where this behavior is especially common and merely all materials reconstruct into oxyhydroxides or related structures, [16,18–25] while non-oxide anions leach as oxyanions. [26,27] These observations are consistent with the Pourbaix diagrams of the respective elements, [28] and numerous reviews on the topic have been written. [16,18–22,25,29–31] Furthermore, the active transition metals dynamically dissolve and redeposit during electrocatalytic processes. [32] This dissolution and redeposition lead to the mixture of separated phases, e.g., an iron-based catalyst deposited on nickel foam will most likely form NiFeOOH. This dynamic behavior strongly limits the design dimensions of chemists. Furthermore, it makes it challenging to identify the active structure, surface/interface, and site of the catalyst, which are essential inputs for meaningful DFT calculations. In this regard, heterostructure electrodes are exceedingly complex. From our point of view, understanding heterostructured systems and obtaining meaningful DFT calculations is extremely challenging with the current electrochemical and analytical methods. Thus, deducing complex interface-related hypotheses for enhanced activities is often misleading, as fundamental aspects commonly remain elusive, e. g., (i) is there an intrinsic change in activity or a surface area effect compared to less complex references, (ii) which phase/surface/interface is responsible for catalysis, (iii) did new phases form under operating conditions, (vi) what is the active site…? This perspective summarizes challenges that must be met before complex hypotheses on activity enhancements can be deduced and introduces a systematic pathway providing solutions to these challenges. It applies to electrocatalysis in general and uses the OER and heterostructures as particular examples.

2. Understanding electrocatalysts: challenges and a systematic pathway to resolve them

This section is divided into three parts, which all contain one schematic figure with four key points (Figs. 1, 3, and 5). These three figures describe systematic pathways with four consecutive points to obtain meaningful DFT inputs and results. The first deals with determining the investigated catalysts' activity enhancement compared to references, especially with the separation of intrinsic activity enhancement versus enhancement in the number of active sites. The second discusses determining the atomic and macroscopic structure of the whole electrode comprising phases during catalysis. The third aims to identify the active sites and reaction mechanism to obtain a meaningful DFT input.

2.1. Intrinsic activity versus number of active sites/surface area

Fig. 1 shows four points to determine if the investigated catalyst's intrinsic active per active site has changed compared to references. The *first point* is to choose suitable references. The references should be simple, widely applied compounds containing the same active elements as the reported catalyst. Ideally, they have the same surface area and have been made with the same synthetic protocol. It is important to note

here that even phases of different transition metals made with the same synthetic protocol can have entirely different morphologies and surface areas. When multiphase systems are investigated, every single phase should be used as a reference, and phases that likely form during catalysis. In this regard, we recommend looking at the Pourbaix diagrams of each element of the investigated new material. If there are nonsoluble, thermodynamically stable phases, those should be used as references, e.g., for the alkaline OER, cobalt oxyhydroxide for any cobalt-containing material. Furthermore, some constituting elements will mix through dissolution-redeposition processes. For example, suppose a heterostructure with a cobalt- and an iron-containing phase is studied for the OER. In that case, a bimetallic single-phase cobalt-iron reference is also required, as such a phase will form to some extent during catalysis through dissolution and redeposition. [32] Additionally, a widely applied and highly active reference material should be included that does not have to share the same active elements, e.g., for alkaline OER, a simple nickel-iron oxyhydroxide, for acidic OER, iridium dioxide, or for the HER, metallic platinum. [33–35] The reference's surface area, morphology, and appearance (powder, self-supported electrode, thin film…) should be as similar as possible to the main compound. The following three points of Fig. 1 must be performed with all reference materials.

The *second point* is to determine the geometric current density. The electrode's surface likely behaves dynamically during the reaction conditions, and it can take some time until a stable state is obtained. Thus, it is essential to expose the electrode to the reaction conditions for prolonged times (up to days) until all reconstruction processes are completed, allowing the measurement of activity metrics under steady-state conditions. This prolonged exposure is crucial. It can be accomplished by different methods like cyclic voltammetry of chronopotentiometry or -amperometry (only linear sweep voltammetry is not sufficient). A critical aspect is always to perform the same activation before any electrocatalytic or analytical data is acquired. Another essential aspect is that a reliable way to determine the pH and reversible hydrogen electrode potential is chosen. [36,37] Furthermore, the activity comparison should be performed in a regime where mass transport of the substrate is not a limiting factor. Otherwise, the performance will mainly depend on the surface area and not on the intrinsic activity. [38] To do so, high substrate concentrations, stirring if possible, and suitably low current density should be chosen. [38].

The *third point* is quantifying the number of active sites or at least the surface area of the reported catalyst and the references. [39] Especially precise active site quantifications have not been achieved even for some of the simplest systems. Nevertheless, it is frequently possible to determine quantities proportional to the number of active sites, such as the number of sites that can change their redox state or the surface area. The number of redox active sites is especially important for OER-active oxides and can be obtained electrochemically by applying a potential above and below a redox transition (chronoamperometry or potentiodynamic methods such as cyclic voltammetry). [17,40] If no substantial
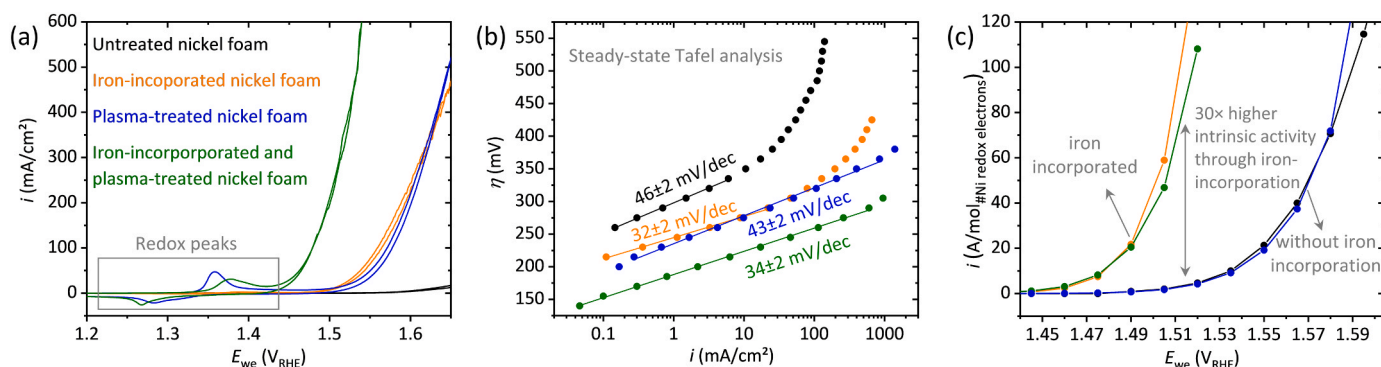
Fig. 2. Literature example for Fig. 1. Cyclic voltammograms (a), Tafel slopes (b), and normalization of the potential-dependent current density (c) by the number of electrons transferred in the redox peaks (grey box of (a)) of four samples: (i) untreated nickel foam, (ii) iron-incorporated nickel foam, (iii) plasma-treated nickel foam, and (iv) nickel foam that was first plasma-treated and then iron incorporated. All data is taken from reference [40] and *iR*-compensated. (a) was obtained with a scan rate of 5 mV/s. (b) and (c) were obtained by holding a constant potential for at least 3 min per data point to record steady-state data.

additional electrochemical processes take place in the investigated potential region, the transferred charge can be assigned to the redox activity and the number of redox-active sites determined. Ideally, this method is combined with analytics resolving the bulk oxidation state, such as in-situ X-ray absorption spectroscopy. This approach has recently been used to investigate if an electrocatalyst is surface or bulk active. [17] However, not all active sites have isolated redox peaks suitable for such a determination.

Alternatively, the surface can be measured. Unfortunately, such measurements are often highly challenging and ambiguous. Many methods have been proposed such as (i) hydrogen underpotential deposition, (ii) carbon monoxide stripping, (iii) underpotential deposition, (iv) atomic force microscopy, or (v) electron microscopy. [39] All these methods can only be applied to particular systems, e.g., the first three are limited to certain noble metals and the last two to thin films or particular monodispersed morphologies. [39] A more broadly applicable but also controversial method is to determine the double-layer capacitance, which is often assumed to be proportional to the electrochemical active surface area. [39] This determination can be performed at a potential where no electrocatalysis takes place. However, many electrocatalysts change their conductivity, morphology, and chemical nature under reaction conditions. Therefore, such measurements are often not meaningful, e.g., iron, cobalt, and nickel oxyhydroxides are not conducting at potentials below their redox and OER onset. [41,42] Thus, no double-layer determination can be performed in this region. Impedance-based methods have been proposed for in-situ measurements, but we have found that the fitting of the impedance spectra can be ambiguous for complex systems. [42,43] Furthermore, the double layer might be too large (insensitive) to determine the surface area of nanostructured materials, and even if it is determined correctly, it must not necessarily be proportional to the number of active sites. Nitrogen adsorption isotherm methods are another more widely applicable method to determine the surface area. However, applying them to the reconstructed catalyst is challenging, as the measurement requires a lot of sample (surface area). In conclusion, there is still no straightforward way to determine the number of active sites or the surface area of electrocatalysts, and individual solutions for each system are required. [39] These solutions likely involve more than one method.

The *fourth point* is to determine parameters that reflect an intrinsic activity. Ideally, this would be the turnover frequency. However, as the number of active sites is unknown in most cases, other metrics that are easier to determine must be used. The most applied one is the Tafel slope. The Tafel slope depends on the mechanism of the catalyst. Mostly, the Tafel slope is insufficient to determine the mechanism or active site. Nevertheless, it can be used to determine if two catalysts operate with the same mechanism and active site. This similarity is strongly indicated when both systems have the same Tafel slope. In such a scenario, better

electrocatalytic performances are caused by different numbers of active sites. One of the continuous and severe problems of Tafel slope determination in the electrocatalysis literature is that potentiodynamic methods (linear scan or cyclic voltammetry) are often used, leading to not purely kinetic Tafel slopes influenced by additional parameters like catalyst oxidation, double layer charging, or reconstruction of the material. [44] Such Tafel slopes cannot be used for mechanistic insights. We note that there are further sample-specific problems that can hinder the determination of an intrinsic Tafel slope, such as mass and electron transport. In this regard, low loadings and moderate current densities can be beneficial for the Tafel slope determination.

When the four steps of Fig. 1 have been followed, for a set of reference compounds and the reported catalyst, the geometric current density at the same potential, an at least qualitative difference in the number of active sites, and changes in the Tafel slope should be known for the new electrocatalyst. This data is a suitable foundation to determine if the reported catalyst has a higher geometric current density because of an intrinsic change of the active sites or only their number. From our point of view, in the OER literature, the vast majority of reports deal with changes in the number of active sites. If only the number of active sites changed compared to a well-known system, determining adsorption energies by DFT is not relevant for experimentally focused reports.

Fig. 2 shows a suitable example where the number of active sites and the intrinsic activity enhancement could be separated. Fig. 2's data is taken from a recent study by us, [40] where the surface area and number of available active sites of nickel foam were enhanced with an in-liquid plasma approach. Four samples were investigated for the alkaline OER: (i) untreated nickel foam, (ii) iron-incorporated nickel foam, (iii) plasma-treated nickel foam, and (iv) nickel foam that was first plasma-treated and then iron incorporated. Fig. 2a shows the cyclic voltammograms of the four samples, which reveal that both processes, plasma treatment and iron incorporation, increase the geometric current density. Fig. 2b shows the respective Tafel slopes obtained by the steady-state methods. [44] The plasma treatment does not change the Tafel slope, while the iron incorporation decreases its slope. Thus, the activity enhancement through iron incorporation is intrinsic, while the plasma treatment increases the number of active sites without changing the turnover frequency. Fig. 2c shows the normalization of the potential-dependent current density by the number of electrons transferred in the redox peak (Fig. 2a grey box). With this normalization, the samples with the same Tafel slope have the same activity, which means that the number of electrons transferred in the redox peak is proportional to the number of available active sites. Thus, the intrinsic activity enhancement by the iron incorporation (30 times) and the enhancement of the number of active sites by the plasma treatment (40 times) could be separated and quantified. A similar approach could recently be used to
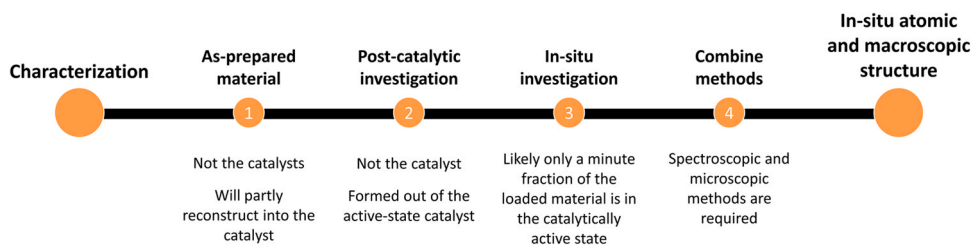
Fig. 3. In-situ characterization. Four steps to characterize the atomic and microscopic structure of all phases present on the electrode during catalysis. Even when the electrode's in-situ structure is known, there are still numerous possibilities for the active structure and site in most cases.

identify if cobalt oxyhydroxides are only OER-active at their surface or throughout the bulk [17].

2.1.1. Faradaic efficiency and product selectivity

Section 2.1 focused on activity differences of electrocatalysts. Another crucial aspect is faradaic efficiency and product selectivity. [45] Current density at a specific potential is a suitable parameter to compare activities. However, this comparison is only meaningful if all electrons are used for the same process, e.g., for the OER or HER, it must be checked if the number of passed electrons is consistent with the evolved amount of oxygen or hydrogen gas (faradaic efficiency). For reactions involving more complex (organic) molecules, multiple products can be formed from the reduction or oxidation of the same substrate. This aspect will not be discussed in depth herein. However, in such cases, the comparison is less straightforward, and it must be carefully analyzed if a change in product selectivity is caused by an intrinsically different active site or by an external parameter such as surface area.

2.2. The in-situ atomic and macroscopic structure of the electrode

Fig. 3 shows four points to characterize all electrode-comprising phases' atomic and macroscopic structures during electrocatalysis. In the *first point*, the as-prepared material must be characterized. Compared to the following points, such as the in-situ characterization, this characterization can be more straightforward. However, the as-prepared material (or its surface) is mostly not the active catalyst. Thus, it is not a meaningful DFT model. Furthermore, determining the interface facets can be highly challenging for heterostructured materials, and every system's characterization requires an individual combination of methods and solutions.

The *second point* is the characterization of the electrode after catalysis. It is again crucial to consistently apply the same electrocatalytic treatment until the catalyst has completed its reconstruction before performing the characterizations. This post-catalytic investigation is often more challenging than the one of the as-prepared material, as less than a milligram of (pre)catalyst is usually loaded, and thus, a limited sample is available. Furthermore, it might be hard to detach the material from the electrode, and the system's complexity often increases as new phases and interfaces form during catalysis. Nevertheless, post-catalytic characterizations can give valuable insights into the structure of the active catalyst. It can be determined if the material underwent an irreversible reconstruction process and formed a new material. Often well-known, relaxed-state catalysts are found after catalysis, e.g., a cobalt oxyhydroxide after the OER formed from a cobalt-based material like cobalt sulfide. In such cases, in-situ reports of other publications can be used to get an idea of the active-state catalyst structure. Furthermore, post-catalytic characterizations can identify if elements have leached and if phases have mixed. Thus, they are useful for planning suitable in-situ characterization experiments and developing first hypotheses on the in-situ structure.

The *third point* is the application of in-situ or even operando methods. Those can directly investigate the active catalyst but are more challenging to perform. However, in-situ methods often do not produce data that originates mainly from the active catalysts' structure, as probably only a minute part of the sample is responsible for the catalytic activity, e.g., only the surface atoms or only a minute reconstructed part of the material. Furthermore, applying in-situ methods mostly requires a variation in the experimental setup. These variations can affect the formed material, e.g., a change of the redox behavior depending on the film deposition method and the electrode substrate, as the fraction of anodically wired sites changes.

For conclusiveness, a *fourth overarching point* must be considered: the combination of methods. A fundamental aspect is that microscopic methods and spectroscopic methods are combined. The first provide information on a local specific part (often less than a ppb) of the sample, and the second provide averaged information on a large set of atoms. In this regard, assigning an activity to a specific interface probed with transmission electron microscopy (TEM) image is ambiguous, as this image represents only a ppb or much less of the whole sample. There might be dozens of other interfaces. As we have measured hundreds of hours of TEM ourselves, we know that it is possible to find almost everything one wants in a sample, especially when heterostructures that have reconstructed during catalysis are investigated. Additionally, one or two interplanar spacings with usually 2–3 significant digits, e.g., 2.1 Å not 2.134 Å, determined by high-resolution TEM do not allow a conclusive assignment of a phase, its orientation, or even interface. Furthermore, the sample on the TEM grid, which is electron transmissive, might not be representative of the material on the electrode's surface. Therefore, to be conclusive, microscopic and especially TEM findings must be supported by additional spectroscopic methods. There are currently no straightforward methods for the spectroscopic identification of a particular interface in a heterostructured system. Thus, in most cases, a conclusive post-catalytic and in-situ characterization of as-prepared, multiphase electrodes that additionally reconstruct during catalysis is not possible or at least beyond the scope of most reports. Nevertheless, such interface assignments with TEM images have become common practice, and novel hypotheses for activity enhancements are often concluded on this unsteady basis.

Another central aspect is that methods probe different areas of the sample, they can be bulk-sensitive or surface-sensitive, and for microscopic investigations, the sample preparation can cause a specific selection of the material. Considering that only a minute fraction of the loaded material might be catalytically active, e.g., only a subnanometer surface layer, various methods must be combined to make sure no phase is overlooked. In this regard, we have recently faced a vivid example when applying a non-electron-conducting cobalt borophosphate precatalysts on a fluorine-doped tin oxide (FTO) glass plate for the OER. [13] The cobalt borophosphate reconstructed to cobalt oxyhydroxides, but this reconstruction took only place at the interface with the FTO and most of the borophosphate remained untransformed. Thus, a sandwich was formed with the thin active phase in the center and FTO and intact cobalt borophosphate at the bottom and top, respectively. Post characterization using TEM, X-ray photoelectron spectroscopy, Raman spectroscopy, and X-ray diffraction (XRD) gave the same result before and after catalysis, as all only investigated the intact borophosphate phase covering the newly formed oxyhydroxide. Only X-ray absorption spectroscopy, which is bulk sensitive and suitable for amorphous materials, could detect the oxyhydroxide responsible for catalysis. This example
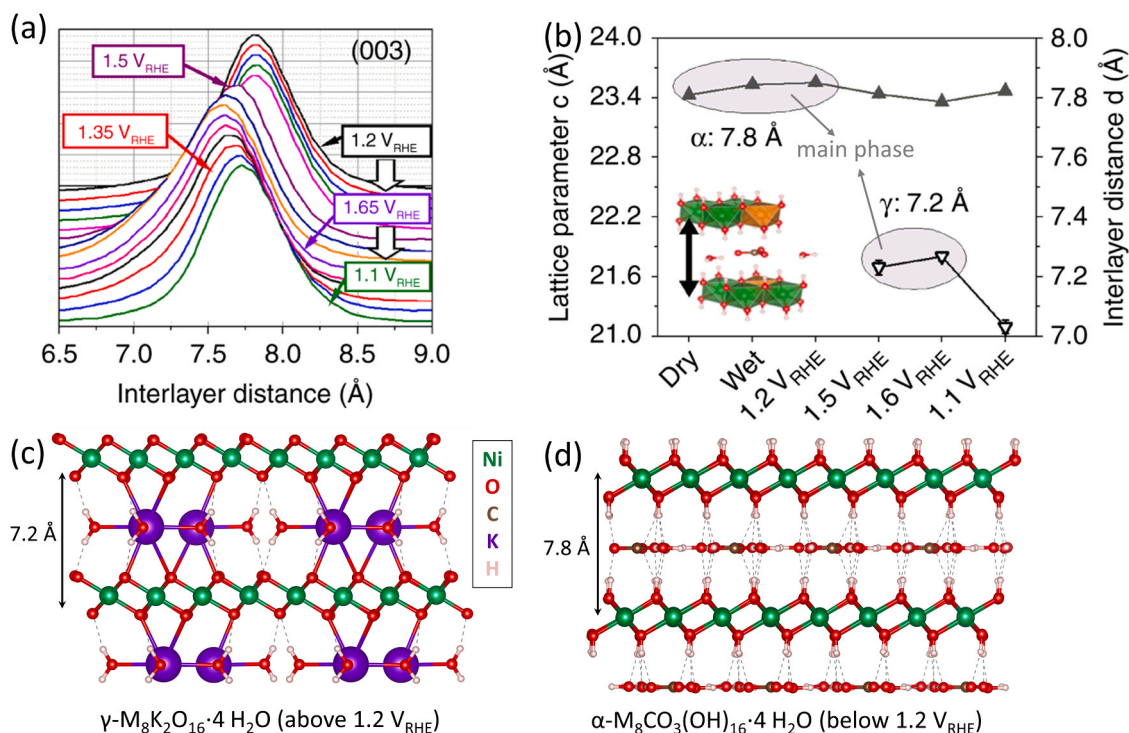
Fig. 4. **Literature example for** Fig. 3. (a) XRD peak related to the interlayer distance of nickel(-iron) oxyhydroxide in aqueous potassium hydroxide at various potentials. (b) the respective interlayer distances obtained by Rietveld refinement for an alpha and gamma oxyhydroxide phase. The grey ellipses mark the main phase at the respective potential. (c) The structure of nickel(-iron) oxyhydroxides (M = Fe, Ni) below (carbonate intercalated, M(II/III)) and above 1.2 V_{RHE} (potassium intercalated, M(III/IV), during OER potentials), as proposed by Dionigi et al. All data and (a) and (b) have been taken from reference [46]. (c) and (d) are reproductions of reference [26].
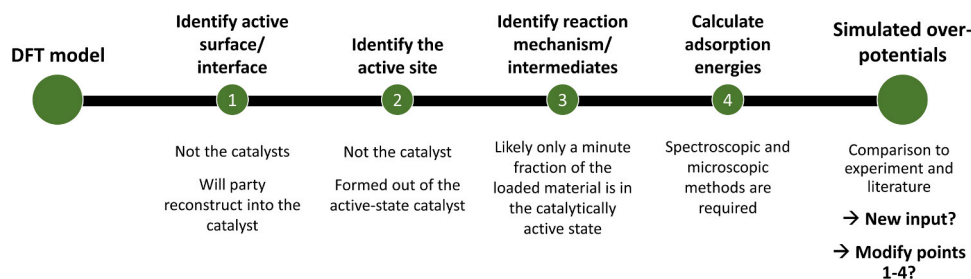
Fig. 5. **DFT input model.** Four points to simulate overpotentials using a suitable DFT input model. Due to the myriad of possibilities, these four points likely must be repeated multiple times until practically relevant overpotentials are simulated, considering the experimental results and previous literature reports.

proves the necessity of combining various analytical methods to gain a conclusive understanding.

Fig. 4 shows a suitable example for the in-situ characterization of electrocatalysts. It is taken from reference [46] published in 2020. This study by Dionigi et al. revealed the structural changes of iron-incorporated nickel and cobalt oxyhydroxides in alkaline electrolytes during the OER. Fig. 4a shows the XRD peak related to the interlayer distance of these phases, and Fig. 4b displays the respective interlayer distances. This data could reveal for the first time that these oxyhydroxides form carbonate intercalated species at a potential below 1.2 V_{RHE} (Fig. 4c) and potassium intercalated ones above this potential and under OER conditions (Fig. 4d). This refined structural knowledge was used for new OER DFT simulations. [46] Nickel and cobalt oxyhydroxides had been investigated for almost a century for the OER before Dionigi's work. Nevertheless, their in-situ structure had not been discovered until then. This shows how challenging it is to obtain precise in-situ structures.

2.3. Selecting meaningful DFT input models

Fig. 5 shows four points to simulated overpotentials via a meaningful ab initio (mostly DFT) model after an intrinsic activity enhancement has been identified and the electrode has been conclusively in-situ characterized. It does not discuss technical challenges in performing the DFT simulations itself and the drawback that mostly thermodynamics without transition states are considered. [47–49] The points of Fig. 5 can be outstandingly challenging due to the multiple phases, surfaces, interfaces, and various chemical environments of the potential active sites. It will often remain an iterative process, where specific sites and mechanisms are repeatedly assumed and the respective calculations performed. These results must then be critically evaluated and compared to the experimental values and previous literature reports.

In the *first point* and *second point*, the active surface or interface and active site within this surface or interface must be identified. This identification is challenging even for a single-phase material, as only atoms at certain facets and surface terminations or defects might drive catalysis. In systems with higher complexity, numerous interfaces,
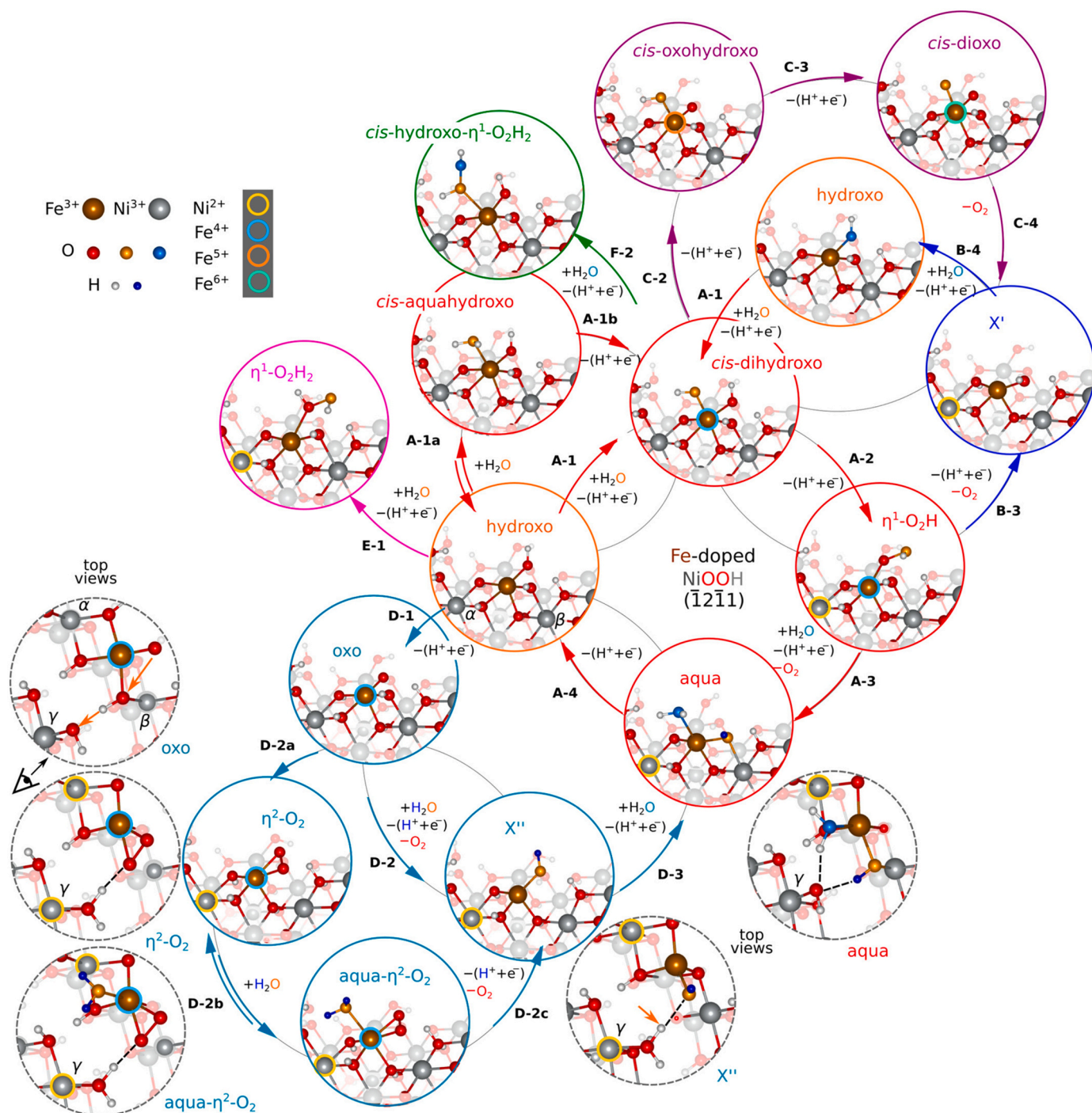
Fig. 6. Literature example for Fig. 5. OER mechanisms on iron-doped beta nickel oxyhydroxide on the [$\bar{1}2\bar{1}1$] surface investigated in reference [50]. Different intermediates on the iron-centered active site are shown as ball-and-stick models. Four pathways with different key intermediates were studied: (i) η^1-O$_2$H route (Pathways A and B), (ii) cis-dioxo route (C), (iii) oxo route (D), and (iv) dihydrogen peroxide (η^1-O$_2$H$_2$) route (E and F). This is a reaction network for a single active site of one surface termination of a single-phase system. There are multiple possible active sites per surface and multiple surfaces per phase. For heterostructures, there are additionally multiple interfaces for each surface. Thus, the number of possible OER pathways that must be considered to deduce a meaningful model is enormous.

surface reconstructions and terminations, and defects lead to countless possibilities of potential chemical environments of active sites. Therefore, identifying the real active site remains an iterative process. For an educated guess, chemical intuition must be paired with suitable single-phase reference experiments and analytics such as isotope labelling or in-situ methods tracking a structural change concurrent to the catalytic onset. Also, ab initio calculation can be used to find the thermodynamically most stable surface or interface. Nevertheless, the most stable

surface or interface might be comparably inactive and thus insignificant for catalysis. [50] Furthermore, a surface or interface identified via TEM microscopy could be used as input. However, multiple other interfaces in the material might be missed, as the method is unsuitable or as they are severely more seldom. Thus, it is challenging to completely rule out surfaces, interfaces, and active sites by theoretical or experimental investigations, leaving numerous possibilities.

In the *third point*, after an active site has been chosen, a reaction

mechanism with intermediates must be proposed. In most cases, there will not be experimental evidence for all intermediates, and again only hypotheses can be raised. Furthermore, it is essential to note that just because a particular species is observed on the catalyst's surface, it is not necessarily part of the desired catalytic pathway.

The *fourth point* is the calculation of the assumed intermediates' adsorption energies. In most theoretical studies, no transition states are considered. Thus, thermodynamical limits of the overpotentials are obtained, assuming that the Brønsted−Polanyi−Evans relation holds. [47–49] These overpotentials must be compared to the experimental ones. If they are substantially larger, the assumed active sites or reaction mechanisms are likely incorrect. Then, new assumptions must be made and the process of Fig. 5 repeated. In this regard, we note that even for high-quality DFT calculations of adsorption energies, intrinsic errors of 0.2 eV can be expected. [51] However, the reported discrepancies are regularly much larger, [4,52] and qualitative trends are extracted from adsorption energies, e.g., the thermodynamic overpotential on the interface-containing model is lower than that of the two single phases. However, if the overpotential for the interface compound does not match the experimental one at all, the calculations only prove that the assumed model is false, and from our point of view, even such qualitative trends must not be deduced. Furthermore, for simple monometallic NiOOH and CoOOH, overpotentials well below 500 mV have been calculated, and for bimetallic NiFeOOH, even well below 200 mV. [50, 53] If DFT calculations on multimetallic heterostructure yield significantly larger overpotentials than those obtained for these simple systems, their meaningfulness is highly questionable.

Fig. 6 shows a suitable example of the complexity of Fig. 5's points. It is taken from reference [50]. Fig. 6 shows simulated reaction mechanisms only for the $[\bar{1}2\bar{1}1]$ surface of iron-doped beta nickel oxyhydroxide. It represents a minute part of the complexity of the system, as only one surface and one active site among numerous is considered. Thus, a similarly extensive network of reaction pathways should be studied for every surface and every active site on such a surface. Furthermore, the active site might comprise more than one metal center and ligands might be redox-non-innocent. These considerations show the tremendous number of possibilities, even for such a simple single-phase system. For heterostructured systems with interfaces, the complexity is multiple times larger. Thus, we anticipate that rather hundreds than a single DFT study is required to provide a conclusive understanding of novel multiphase catalysts. From our point of view, many reports do not account for this complexity sufficiently, especially if mainly experimental reports are spiced up with brief DFT investigations.

3. Conclusion

With thousands of reports per year on the most prominent electrocatalysis topics, it becomes more challenging to discover new fundamental aspects. A perhaps natural reaction of the community to generate novelty is to increase the complexity of the electrocatalytic systems, which might even be required to achieve optimal performance. However, the high complexity paired with the dynamic behavior of materials' surfaces during electrocatalysis makes it extremely challenging to understand such systems, especially as catalysis potentially takes place at a minute part of the electrode, e.g., at the surface, an impurity, a defect, or a particular interface. This perspective presents a pathway to understanding fundamental aspects of such systems and obtaining meaningful DFT input models, which include the fabrication of suitable references, differentiation between enhanced intrinsic activity and number of active sites, the conclusive characterization of the whole system during electrocatalytic operation, the identification of a suitable active surface, active interface, active site, and reaction mechanism and the critical comparison of the DFT results with experimental values. We anticipate that following this pathway is a potential solution to meet the complexity.

However, this perspective mainly shows the enormous challenges of understanding electrocatalysts, especially when they are heterostructures. It is often not possible to conclusively understand a system with state-of-the-art methods, in particular within the scope of one report. Therefore, no meaningful input for DFT calculations can be obtained, especially for heterostructured systems with countless surface terminations, potential interfaces, and potential chemical environments for the active sites. Thus, from our point of view, if the herein-described fundamentals are not fully clarified, it is harmful to postulate a complex (interface-related) hypothesis to explain the observed electrocatalytic performances. It might be a misconception and pretentiousness of the current academic culture that a manuscript is less valuable if the authors clearly state that multiple aspects remain unanswered and cannot be fully explained. Nevertheless, this is mostly reality comparing the complexity of this field and the currently available methods. Thus, we think that more reports should straightforwardly write what is unknown/unexplainable, and reviewers should appreciate this, especially when complex systems are developed whose catalytic performances are significant for the community.

CRediT authorship contribution statement

J. Niklas Hausmann: Conceptualization, Writing – review & editing. **Prashanth W. Menezes**: Conceptualization, review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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